

N68-16344

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

*Technical Report 32-1227*

*The Status of Monopropellant Hydrazine Technology*

*T. W. Price*

*D. D. Evans*

FACILITY FORM 602

16344	(ACCESSION NUMBER)		(THRU)
24	(PAGES)		(CODE)
CI-92742	(NASA CR OR TMX OR AD NUMBER)		27 (CATEGORY)

**JET PROPULSION LABORATORY  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
PASADENA, CALIFORNIA**

February 15, 1968

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

*Technical Report 32-1227*

*The Status of Monopropellant Hydrazine Technology*

*T. W. Price*

*D. D. Evans*

Approved by:



D. F. Dipprey, Manager  
Liquid Propulsion Section

**JET PROPULSION LABORATORY  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
PASADENA, CALIFORNIA**

February 15, 1968

**TECHNICAL REPORT 32-1227**

Copyright © 1968  
Jet Propulsion Laboratory  
California Institute of Technology

Prepared Under Contract No. NAS 7-100  
National Aeronautics & Space Administration

~~PRECEDING PAGE BLANK NOT FILLED.~~

### **Acknowledgment**

The authors would like to acknowledge the cooperation of the Hamilton-Standard Division of United Aircraft Corp., the Marquardt Corp., the Rocket Research Corp., the Shell Development Co., and TRW Systems for permission to reproduce data and for discussing various technical areas with us.



## Contents (contd)

### Figures

1. Micropore surface area vs run time for Shell 405 catalyst (20-30 mesh) . . . . .	4
2. Theoretical characteristic velocity and adiabatic gas temperature of monopropellant hydrazine . . . . .	6
3. Theoretical vacuum specific impulse of monopropellant hydrazine . . . . .	6
4. Steady-state axial profiles in a catalyst bed . . . . .	7
5. Steady-state axial profiles of reactant concentrations in a catalyst bed . . . . .	7
6. Ignition delay vs the reciprocal of bed temperature . . . . .	11
7. Characteristic reactor response vs chamber pressure . . . . .	12
8. Injector head temperature as a function of duty cycle . . . . .	13
9. Effect of pulse width on specific impulse . . . . .	14
10. Effect of pulse number and pulse width on specific impulse . . . . .	14
11. <i>Mariner C</i> post-injection propulsion system schematic . . . . .	15
12. <i>Ranger-Mariner</i> monopropellant hydrazine 50-lbf thrust rocket engine (nonspontaneous catalyst) . . . . .	16
13. <i>Mariner IV</i> fuel tank pressure increase as a function of flight time . . . . .	17
14. <i>Mariner 1969</i> spontaneous catalyst 50-lbf thrust rocket engine . . . . .	18

~~PRECEDING PAGE BLANK NOT FILMED.~~  
~~PRECEDING PAGE BLANK NOT FILMED.~~

## Contents

<b>I. Introduction</b> . . . . .	1
<b>II. Hydrazine Properties</b> . . . . .	2
<b>III. Catalysts for Hydrazine Decomposition</b> . . . . .	3
A. Nonspontaneous Types . . . . .	3
B. Spontaneous Types . . . . .	3
<b>IV. Catalytic Reaction Chambers</b> . . . . .	5
A. Continuously Operated Thrust Producing Devices . . . . .	7
1. Throttling . . . . .	8
2. Problem areas . . . . .	8
B. Performance of Continuously Operated Devices . . . . .	9
C. Intermittently Operated Thrust Producing Devices . . . . .	10
1. Start transient . . . . .	10
2. Catalyst bed lifetime . . . . .	12
3. Heat transfer to the propellant feed system . . . . .	12
D. Performance of Intermittently Operated Thrust Producing Devices . . . . .	13
E. Gas Generators . . . . .	14
<b>V. Monopropellant Hydrazine Thruster Use on Flight Systems</b> . . . . .	15
A. <i>Ranger-Mariner</i> . . . . .	15
B. <i>Mariner 1969</i> . . . . .	17
C. <i>Intelsat</i> . . . . .	17
D. <i>Transtage</i> . . . . .	17
E. <i>ATS-C</i> . . . . .	17
F. <i>NRL Satellite</i> . . . . .	18
<b>VI. Conclusion</b> . . . . .	18
<b>References</b> . . . . .	19

## Table

1. Some physical properties of hydrazine . . . . .	2
--	---



## Abstract

The use of hydrazine as a monopropellant for thrusters and gas generators has several outstanding advantages. The associated systems are simpler, as compared to bipropellant systems, and the exhaust products are *clean* and relatively cool, allowing utilization of simple, radiation-cooled decomposition chambers. The development of the Shell 405 catalyst, which spontaneously initiates hydrazine decomposition at room temperature, has greatly increased the interest in monopropellant hydrazine systems.

This report gives a brief account of the history of hydrazine as a monopropellant, as well as a few comments on the handling and physical properties of the propellant. The major emphasis, however, is given to a comprehensive survey of the current status of this technology, including catalyst availability and handling, reactor design and operation, system considerations, and the limitations and problems of monopropellant hydrazine. The current and anticipated applications are described, and a brief account of non-propulsion applications is included. Finally, current work relative to new catalysts and propellant additives is summarized.

# The Status of Monopropellant Hydrazine Technology

## I. Introduction

Rocket system designers have often longed for a magic liquid which, upon opening a single valve to a simple "decomposer," would instantly change state into a clean, energetic gas that could then be used to do work—propel or stabilize a vehicle, pump liquids, drive turbomachinery, etc. Monopropellant hydrazine systems, particularly those using Shell 405 catalyst, are currently the closest thing to such a dream. The purpose of this paper is to acquaint a non-specialist with the current status of this technology. Little new data will be presented; rather, the intent is to discuss what is known, as well as what is *not* known, the existing applications, and the potential of this technology.

The Germans used a fuel mixture of hydrazine-hydrate in methyl alcohol (B-Stoff) with hydrogen peroxide as the oxidizer for the power plant of their manned interceptor ME-163. As anhydrous (i.e., less than 5% water) hydrazine became available, it was studied extensively in this country, initially by JPL in the late 1940s, for potential usage as either a bipropellant fuel or as a mono-

propellant (Refs. 1 and 2). It was found that homogeneous, thermal decomposition of hydrazine proceeded very slowly, requiring a residence time of about 35 ms that corresponded to a characteristic length  $L^*$  of about 800 in., far too large to be practical in most applications (Ref. 3).

Subsequent work evolved an efficient catalyst that would sustain hydrazine decomposition if the catalyst temperature could be brought to about 600–800°F initially (Refs. 4 and 5). It was necessary, therefore, to employ a technique that preheated the bed to initiate and sustain decomposition. Preheating methods used include:

- (1) Using electrical or radioisotope techniques.
- (2) Operating in the liquid bipropellant mode for a short period of time.
- (3) Utilizing a liquid-solid hybrid reaction (Ref. 6).

The complications of such techniques, together with early doubts about the safe handling of the propellant, seriously impaired the acceptance of monopropellant hydrazine systems.

Meanwhile, a broad base was being laid at JPL and elsewhere as the feasibility of monopropellant hydrazine devices was demonstrated for a variety of applications, including turbo-alternator power supplies (Ref. 7), liquid guns (Ref. 8), and generated gas pressurization systems (Ref. 9). Simultaneously, industry acceptance of hydrazine-based fuels evolved with the earth-storable ballistic missile development.

Monopropellant hydrazine systems offer several advantages over the bipropellant systems or cold-gas systems. Monopropellant systems are much simpler (which usually implies greater reliability) than a bipropellant system because, obviously, only one fluid system is required and, moreover, the necessity to maintain mixture ratio is not required. But, at the same time, monopropellants offer many of the advantages of bipropellants, such as carrying the desired energy in a compact liquid form, easy on-off control, throttability, etc. Nonreactive, cold-gas systems also offer many of these advantages, but hydrazine offers significantly greater quantities of energy in much smaller and lighter packages. A further advantage of monopropellant hydrazine is its low operating temperature allowing chambers to be built of low cost materials and to be operated with no cooling. So, basically, the advantage of monopropellant hydrazine is energetic simplicity. The added reliability (i.e., simplicity) cannot be overemphasized.

The engineering problems associated with hydrazine systems are few. In the course of this paper, those deficiencies that are unique to monopropellant hydrazine systems will be pointed out, but no attempt will be made to discuss those problems which are common to all liquid propellant systems such as valves, tanks, regulators, etc.

**Table 1. Some physical properties of hydrazine**

Property	Quantity
Molecular formula	$N_2H_4$
Molecular weight	32.04 awu
Density	1.0045 g/cm <sup>3</sup> at 25°C
Melting point	+34.7°F at 1 atm
Boiling point	+236°F at 1 atm
Surface tension	0.004568 lbf/ft at 77°F
Viscosity	0.000605 lbm/ft-s at 77°F
Heat of formation	12.05 kcal/mole
Heat of vaporization	54.0 Btu/lbm at +236°F
Heat capacity	0.737 Btu/lbm-°F at 77°F

The first operational usage of monopropellant hydrazine was in the *Able-4* lunar spacecraft, developed during 1959 by Space Technology Laboratories. Although launch vehicle difficulties prevented the attainment of a successful mission, the *Able-4* 20-lbf thrust hydrazine engine was fired in space as an experiment. Next came the JPL *Ranger* and *Mariner* series spacecraft. All these spacecraft employed a 50-lbf thrust hydrazine engine for postinjection trajectory correction maneuvers. These engines employed the JPL nonspontaneous catalyst and used a bipropellant ignition scheme. Design details of the *Mariner* system will be discussed later.

## II. Hydrazine Properties

At ordinary temperatures and pressures, hydrazine is a clear, colorless liquid with an odor similar to that of ammonia. Some of its physical and thermodynamic properties, pertinent to this discussion, are presented in Table 1. An extensive discussion of hydrazine may be found in Ref. 10.

Hydrazine is miscible only with polar solvents such as water, alcohols, ammonia, and amines. References 11-15 discuss some of these mixtures and their properties.

Hydrazine is thermodynamically unstable with respect to decomposition into the elements and is exothermic when decomposed. It readily decomposes catalytically and also decomposes thermally in the vapor phase if heated to a high enough temperature. In either case, decomposition is accompanied by release of considerable amounts of energy.

Although hydrazine is *easy* to decompose, the initiation energy required is high enough so that it can be handled quite safely. It is not shock sensitive and can be heated to approximately 500°F before thermal decomposition becomes a problem. It should be noted, however, that many materials begin to act as catalysts well below 500°F; therefore, a more practical limit is about 350°F. Mixtures of air and hydrazine vapor are extremely flammable and care must be taken to exclude air from any hydrazine system.

Many common materials of construction are readily compatible with hydrazine. Several of the 18-8 series stainless steels, most aluminums and titaniums, Teflon, and butyl rubber are materials that have been used extensively. Considerable compatibility data are given in Refs.

16 and 17. Hydrazine systems must be free of rust and scale or other contaminants which may act as a catalyst. However, even this is not very stringent compared to the cleanliness requirements for oxygen and fluorine.

One of the principal disadvantages of hydrazine is its relatively high freezing point ( $\sim 35^{\circ}\text{F}$ ). Most military specifications require a freezing temperature of  $-65^{\circ}\text{F}$ . For many applications, the hydrazine freezing point is acceptable, but a lower value would provide an extra margin of safety; this is still an area for much experimentation. The problem is to find an additive that does not adversely affect the desirable properties. For monopropellant applications, mixtures of water, ammonia, and hydrazinium nitrate appear to be most promising.

The long term storage stability of hydrazine has always been in doubt, because of its tendency to undergo heterogeneous catalytic decomposition. At near-ambient temperatures, long duration ( $\sim 4$  yr) storage of hydrazine in aluminum tanks was demonstrated at JPL (Ref. 18). Long term storage in a bladdered titanium tank is discussed in Section V of this report. Relatively short duration ( $\sim 100$  h) storage of hydrazine in titanium vessels at  $293^{\circ}\text{F}$  was also demonstrated at JPL (Ref. 19).

So, while hydrazine is not something to be handled casually, for the rocket industry, which routinely handles chemicals such as liquid oxygen, liquid hydrogen, hydrogen peroxide, nitric acid, fluorines, boranes, etc., hydrazine is relatively straightforward.

### III. Catalysts for Hydrazine Decomposition

The differentiation between nonspontaneous and spontaneous catalysts is somewhat arbitrary and may well vary depending on the interpreter. When hydrazine catalysis is the topic, spontaneous implies three things:

- (1) The decomposition can be initiated while the catalyst and hydrazine temperatures are no higher than  $70^{\circ}\text{F}$ .
- (2) No other energy source is required.
- (3) The time between contact of hydrazine with the catalyst and the initiation of the decomposition process is very short (10–100 ms).

If any of these restrictions are relaxed, then catalysts that ordinarily would be considered nonspontaneous, could be considered spontaneous.

#### A. Nonspontaneous Types

As mentioned previously, hydrazine decomposition must be promoted by catalysis for reasonable sized reactors to be attained. Extensive early work by A. F. Grant (Refs. 3 and 5) evolved a series of catalysts using metallic iron, nickel, and cobalt deposited on an alumina carrier. When 1/8 to 3/16-in. cylindrical pellets of compressed, activated aluminum oxide are used as the carrier, the catalyst is known as JPL Type H-A-3. If higher-strength, but lower surface area, fused aluminum oxide spheres are used, it is designated JPL Type H-7. Both types of alumina carriers are used in the chemical process industry and are readily available. These catalysts are resistant to chemical poisoning (although free carbon or sulfur will act as poisons), have a long shelf life ( $>5$  yr), and are available commercially.\* The use of non-critical metals and a relatively simple manufacturing procedure results in an almost unlimited supply at a modest cost ( $\$2$  to  $\$6/\text{lbm}$ ). Their primary disadvantage, as stated before, is that the catalysts will not spontaneously decompose hydrazine at room temperature.

#### B. Spontaneous Types

Over the years, efforts were expended at JPL (Ref. 3) in searching for a spontaneous catalyst, but with no real success. In January 1962, a search began in earnest when the Shell Development Co. won a NASA competition to attempt to develop such a hydrazine catalyst. The results, reported in Ref. 20, must be considered a true technological breakthrough. This developed catalyst, known as the Shell 405, is not only spontaneous, but is capable of many spontaneous starts. This capability is one of the primary reasons for the interest it has aroused.

The availability of this catalyst has greatly expanded the potential application of hydrazine as a monopropellant. Before the advent of Shell 405, interest in monopropellant hydrazine was centered principally at JPL, but now at least half a dozen industrial concerns are pursuing in-house or contracted programs based on the Shell 405. Both NASA and DOD are now heavily committed to hydrazine systems.

The Shell 405 catalyst is composed of only two components. These are the high surface area ( $160\text{ m}^2/\text{gm}$ ), aluminum oxide carrier and the active metal, iridium. The iridium constitutes slightly over 30% of the total catalyst mass. The actual manufacturing process is classified. The

\*Type Ni 1600 S (Type H-7) and Ni 1601 T (Type H-A-3) are supplied by the Harshaw Chemical Div. of Kiewanee Oil Co., Cleveland, Ohio.

catalyst is currently available in several particle sizes and shapes. The current cost of Shell 405 is about \$2000/lbm, and this cost is one of its major disadvantages. This factor, along with the present fairly limited supply of iridium, restricts its use somewhat. Shell estimates that there is enough iridium currently available to make 1000 lbm of catalyst a year. The current rate of catalyst production is approximately 100 lbm per year. Iridium is presently a by-product of platinum mining, but there are substantial, unexploited iridium deposits in Africa, so that its availability should not necessarily be the limiting factor in preventing major usage of the Shell 405.

As with any rapidly developing field of technology, many potential problem areas are bypassed or explored in only enough detail to solve the current pressing problems. Handling of the Shell 405 catalyst is one of these potential problem areas. For instance, it has been known, since the first introduction of the Shell 405, that it is hygroscopic. Also, upon exposure to air, the catalyst is oxidized as well. What harmful effects these problem areas might create, if any, has been mainly a matter for speculation. It has been evident that, at ordinary ambient temperatures and pressures, the effects were slight.

Small scale reactor work at Aerospace Corporation led to the first realization that there could be a potential vacuum ignition problem. A broader study examining the area of catalyst handling confirmed the Aerospace observations relative to vacuum ignition. These results are reported in Ref. 21 and are based on the five phenomena investigated: exposure of catalyst to vacuum, surface area degradation during reactor operation, exposure to common solvents, oxidation-reduction cycling, low temperature catalyst bed ignition. Summarized briefly, the results and conclusions of Ref. 21 are:

- (1) Appreciable ignition delays may be encountered in a vacuum environment. However, this effect is strongly dependent on reactor design, temperature, and the prior history of the catalyst; thus, the effect cannot be adequately predicted at this time.
- (2) The catalyst surface is reduced very rapidly during the first few minutes of reactor operation, and then changes only slightly thereafter. Figure 1 illustrates this point. Although a properly designed reactor will operate satisfactorily on degraded catalyst, this point is one of the factors that affect ignition delay.
- (3) Exposure to methylene chloride, freon, trichloroethylene, or distilled water has no effect on the

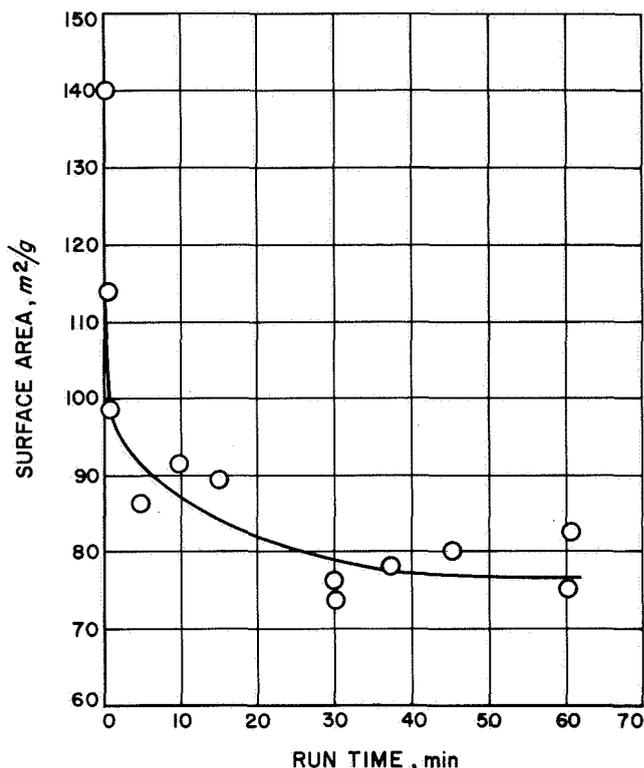


Fig. 1. Micropore surface area vs run time for Shell 405 catalyst (20-30 mesh) (reprinted from Ref. 21)

catalyst. Exposure to alcohol or acetone may lead to a long ignition delay on the first firing following exposure. However, even these two solvents had no permanent effect.

- (4) Cyclic operation of a reactor in a vacuum, followed by exposure to air, revealed no discernible catalyst degradation attributable to the air exposure.
- (5) Catalyst bed temperature has a marked effect on ignition delay, particularly below the freezing point of hydrazine.

Some recent work by the Hamilton-Standard Div. of the United Aircraft Corp. indicates that the ambient pressure effect on ignition delay is associated with freezing of the hydrazine, and not catalyst activity. Their experiment consisted of observing the start transient for different ambient pressures down to  $8\mu\text{m Hg}$  (approximately 0.0002 psia). At  $17\mu\text{m Hg}$ , a noticeable and reproducible change occurred in the ignition delay. They attributed this change to a freezing of a portion of the hydrazine initially introduced into the reactor. The delay then occurs because it takes longer to decompose enough hydrazine to raise the bed temperature.

Although the Shell 405 catalyst has excited the most interest and seems to possess a very good combination of activity and durability, other spontaneous catalysts are available. These catalysts are generally less active, particularly at low temperatures, than the Shell 405 and, in addition, may be less durable. Most of these are described in Ref. 20. However, none have received a great deal of attention and their usefulness is still in question. The military, in particular, has a requirement for lower cost catalysts, even at the expense of longer cold bed response times, less efficiency, etc.

#### IV. Catalytic Reaction Chambers

A hydrazine, catalytic decomposition chamber consists basically of an injector for distributing the hydrazine and a catalyst bed enclosed in a suitable container. (See Fig. 12, a typical reactor.) The injector and the geometry of the catalyst bed may vary widely depending on the purpose of the reactor and the imagination of the builder. Regardless of the design and use, all reactors operate in basically the same way.

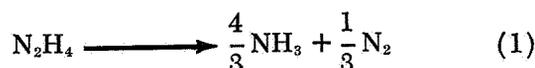
The purpose of the injector is to atomize the liquid hydrazine and to distribute it to the catalyst bed as uniformly as possible. A second objective is to place the maximum amount of catalyst in contact with the hydrazine in as short a time as possible to minimize the start transient time.

Within the catalyst bed, there appear to be four more or less distinct regions. In the bed region nearest the injector, the liquid is vaporized. The energy for this phase change comes from the catalytic decomposition of a small amount of hydrazine. In the next region, moving from the inlet of the bed to the outlet, the heterogeneous catalytic decomposition of the vaporized hydrazine assumes a dominant role. In the third region, hydrazine continues to decompose, but principally in a homogeneous reaction. In the last region, a portion of the initially-formed ammonia is dissociated endothermically to nitrogen and hydrogen. The first three regions occupy only about 10% of the total bed length under steady-state conditions.

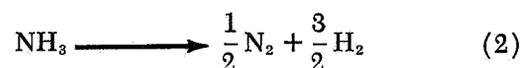
The performance of monopropellant hydrazine reactors can be measured with the usual rocket parameters of characteristic exhaust velocity  $c^*$  and specific impulse  $I_{sp}$ . However, there exists a single parameter, unique to monopropellant hydrazine, to completely specify the performance. This parameter is the amount of ammonia remaining in the decomposition products as these gases

leave the catalyst bed. More commonly, one minus this quantity, or the amount of ammonia that has been dissociated, is used.

To present the significance of this percent-ammonia dissociated parameter, the chemical kinetics of the hydrazine decomposition process will be discussed briefly. The overall decomposition mechanism was represented in Refs. 2 and 5 as a two step process. The first step is the exothermic decomposition of hydrazine into  $\text{NH}_3$  and  $\text{N}_2$ .



This step is followed by the much slower endothermic decomposition of the ammonia:

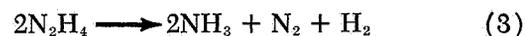


When initiated, the first reaction generally goes to completion, while the second reaction is much slower. Thus, the amount of ammonia dissociated can be controlled by varying the length of the catalyst bed.

Equations (1) and (2) were never intended to represent the details of the decomposition mechanism, but were intended to relate the initial and final chemical species. Thus, the equations could be viewed as a pseudo-stoichiometric relationship. However, Eqs. (1) and (2) have been the source of some confusion, since they imply that a suitably short catalyst bed would result in no molecular hydrogen (i.e., no ammonia dissociated) in the reaction products.

The heterogeneous, hydrazine decomposition process has not been extensively investigated, but the homogeneous process has been studied. References 22 and 23 show that the homogeneous mechanism is much more complicated, as would be expected, than that represented by Eq. (1). Furthermore, hydrogen is produced in a step that does not involve decomposition of ammonia. An analogous situation probably exists for heterogeneous reactions.

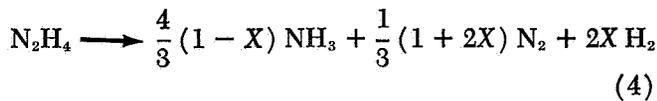
An expression that more closely represents the overall hydrazine decomposition process would be



This process would be followed by further catalytic decomposition of the ammonia.

If Eqs. (1) and (2) are used to represent the decomposition of hydrazine, then there will appear to be at least 25% of the ammonia dissociated regardless of the catalyst bed length. Operating reactors rarely achieve an ammonia dissociation of less than 40% because of other limitations. Thus, the 25% minimum has little practical significance.

For the performance of reactors, Eqs. (1) and (2) are employed (since these equations are widely used by those working in the field and the limitation is generally understood) to obtain



In this case,  $X$  represents the fraction of the originally formed ammonia that is subsequently dissociated. When Eqs. (1) and (2) are combined this way, it becomes obvious why the amount of ammonia dissociated completely specifies the composition of the decomposed hydrazine. Further, it fixes the temperature of the gases,

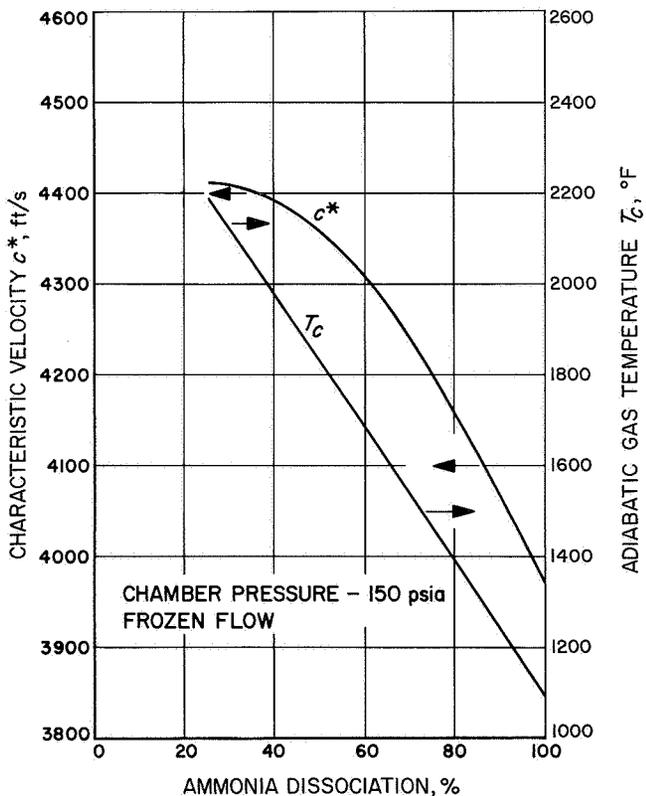


Fig. 2. Theoretical characteristic velocity and adiabatic gas temperature of monopropellant hydrazine

since the energies released in Eq. (1) and absorbed in Eq. (2) are specified in advance. Since the temperature of the decomposition products is rather low ( $\sim 1800^\circ\text{F}$ ) and since the only species present are  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ , all chemical reactions essentially cease at the exit of the catalyst bed, and subsequent gas flow can be considered truly frozen. Thus, specifying the amount of ammonia dissociated also specifies the theoretical reactor performance. Figures 2 and 3 show some examples of theoretical performance as a function of  $X$ . A more extensive collection of theoretical performance calculations can be found in Ref. 24.

It is convenient to subdivide monopropellant hydrazine catalytic decomposition chambers into three categories:

- (1) Continuously operated thrust producing devices.
- (2) Intermittently operated thrust producing devices.
- (3) Gas generators.

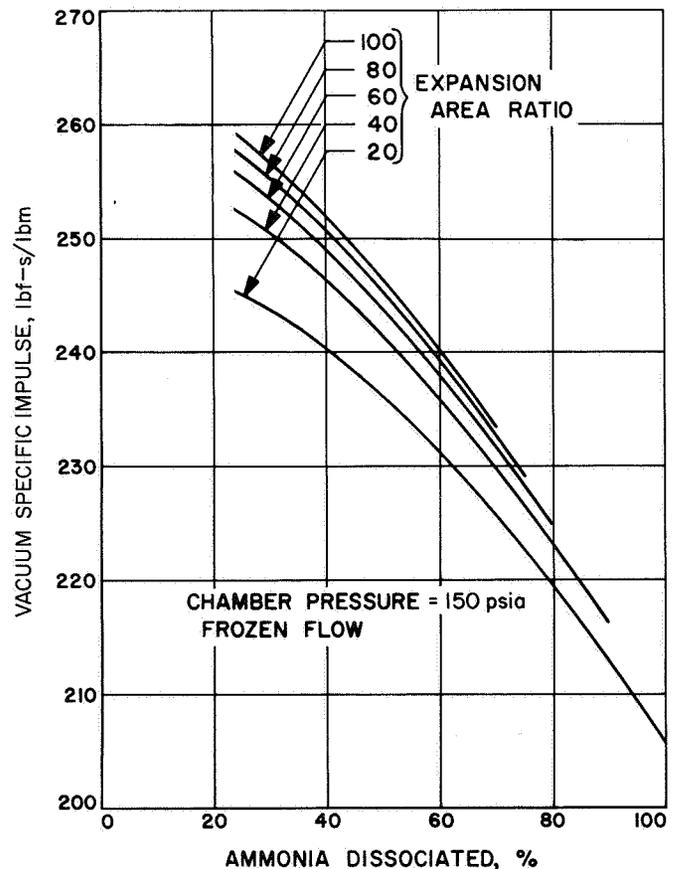


Fig. 3. Theoretical vacuum specific impulse of monopropellant hydrazine

### A. Continuously Operated Thrust Producing Devices

In 1954, A. F. Grant (Ref. 5) published the results of the extensive experimental investigation at JPL on monopropellant hydrazine decomposition chambers. Included in this report are correlations for the prediction of the amount of ammonia that will be dissociated, the pressure drop across the bed, etc. for several nonspontaneous catalysts. This report still serves admirably as the starting point for reactors that use nonspontaneous catalysts, and appreciably reduces the amount of development needed to obtain an optimized reactor.

The first usage of the Shell 405 catalyst was the substitution of it for the nonspontaneous variety in reactors designed according to Ref. 5. The results, while far from discouraging, indicated that the design procedures and

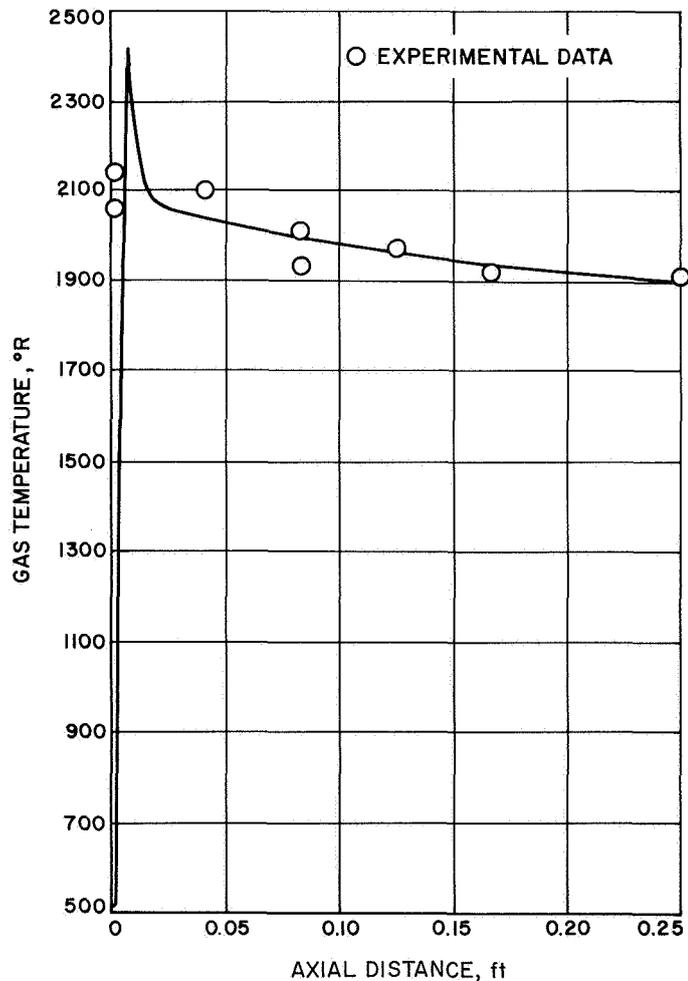


Fig. 4. Steady-state axial profiles in a catalyst bed (reprinted from Ref. 26)

the hardware used with nonspontaneous catalysts were not directly applicable to the more active spontaneous catalyst. Clearly, a new set of design criteria was required. As a result of a competitive bidding, the Rocket Research Corp. was awarded a NASA contract, NAS 7-372, to do an experimental characterization of the Shell 405 catalyst. Volume II of the final report (Ref. 25) is similar to Ref. 5 in that it presents in one place the information needed to design a hydrazine catalytic reactor employing the Shell 405 catalyst.

As a broader approach to characterizing any hydrazine catalyst, the problem is being attacked from the analytical point of view. This work, by the United Aircraft Research Laboratories, is being conducted under NASA contract NAS 7-458. The first year of work is described in Ref. 26. Briefly, the approach and results are as follows. Two computer programs that are based on steady-state and transient models of a reactor system have been developed. These programs have been used to calculate temperature and reactant concentration distributions for various initial bed temperatures, feed temperatures, chamber pressures, mass flow rates, injector locations, and catalyst size distributions. The results have been compared, wherever possible, to available experimental measurements. Generally good agreement between theoretical and experimental results is found. Typical results are shown in Figs. 4 and 5.

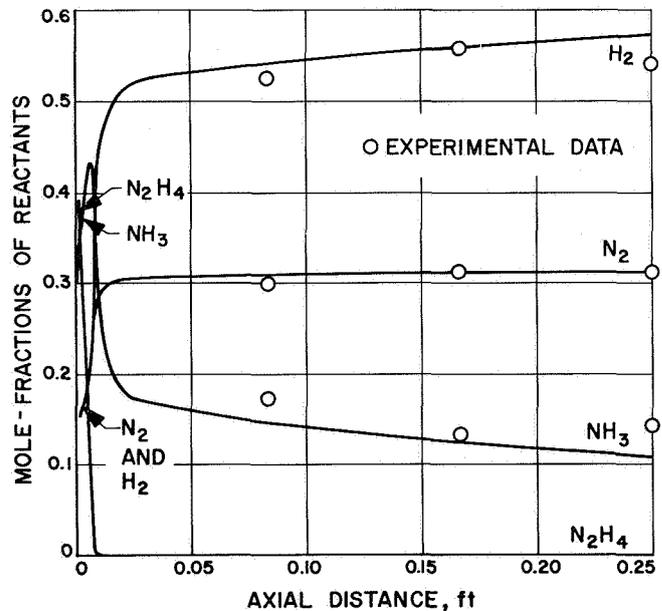


Fig. 5. Steady-state axial profiles of reactant concentrations in a catalyst bed (reprinted from Ref. 26)

Thus, both nonspontaneous and spontaneous catalysts have been well characterized. To date, the largest reactor built and operated as a thruster has produced 300-lbf thrust. However, there is a recent, serious interest in higher-thrust levels, and several detailed designs are completed for reactors that produce 1500 lbf thrust, but hardware is yet to be built. This interest arose principally because of the inherent reliability (i.e., simplicity) of monopropellants. Based solely on the specific-impulse system-weight type of analysis, bipropellants are almost always clearly superior. But when reliability becomes a major consideration and when the total impulse requirements are modest, then monopropellant hydrazine systems are very competitive.

At the other end of the thrust scale, 0.5-lbf thrust seems to be the lower limit for continuously operated devices. There is no inherent reason why such devices must be pulsed, but most applications seem to require it. In a similar vein, most thrusters are operated at chamber pressures less than 300 psia. Again, there is no inherent reason why the pressure cannot be higher; but this low pressure is a natural consequence of the fact that most monopropellant hydrazine reactors are a part of pressure-fed systems. As will be described later, there are other applications for which higher chamber pressures are required.

**1. Throttling.** A requirement for many thruster applications is that of throttling. This is a technology area where monopropellants in general and hydrazine in particular offer several significant advantages over bipropellant rockets. With only one propellant, no mixture ratio problem exists. Although reasonably uniform distribution of the hydrazine over the catalyst bed must be achieved, injection requirements are much less stringent than those for bipropellant engines. Obviously, mixing considerations are nonexistent. Consequently, merely providing a variable pressure drop in the feed system accomplishes the throttling effectively. Several reactors have been throttled in this way over a 10:1 range (50- to 5-lbf thrust).

Several factors tend to limit the throttling range. At the high-thrust end, the bed must be long enough to insure smooth operation; however, as the propellant flow-rate is reduced, the absolute level of performance will drop noticeably even though a large percentage of the theoretical limit is still achieved. This performance drop occurs because a bed sized for high chamber pressure will yield a higher fraction of ammonia dissociation at the low chamber pressure conditions.

Under full-thrust conditions, the bed loading must be limited to avoid an excessive pressure drop across the catalyst bed; this pressure drop could result in crushing the catalyst particles. Bed loading must also be limited so that channeling, the flow of raw hydrazine between catalyst particles or down the walls, does not occur. Channeling results in poor performance and, with nonspontaneous catalysts, may even cool the bed so much that the decomposition reaction cannot be maintained. Channeling does not appear to be a major problem with Shell 405 because of its high reactivity. Channeling and excessive pressure drop must be considered for all reactors, not just those being throttled; however, the design criteria presented in Refs. 5 and 25 take these factors into account.

**2. Problem areas.** As might be expected, because of the rather extensive amount of development work already accomplished, the problems encountered are generally under control. Some of the more important ones are chamber pressure overshoot during the start transient, pressure excursions (*spiking*) during steady-state operation, and loss of catalyst activity.

*a. Pressure overshoot.* The pressure overshoot during startup is a result of the finite time required to initiate the decomposition reaction and, as previously noted, is a strong function of the initial temperature and prior history of the catalyst. During this time period, which can vary from several to over 200 milliseconds, raw hydrazine is accumulated. When the reaction is finally initiated, the released energy is rapidly transferred to the unreacted hydrazine, which then decomposes thermally. This decomposition can be controlled, however.

Probably the best control is to put a thin layer of granular catalyst at the top of the bed. This layer provides a region of high catalyst surface area per unit volume and significantly reduces the reaction initiation time. Reducing the bed loading accomplishes the same objective.

*b. Spiking.* The *spiking* problem is characterized by a sudden change from what appeared to be a state of equilibrium to another steady-state condition. This change can occur anytime from a few milliseconds to a minute after start of the reactor and usually is not a violent change, but it is undesirable, particularly when thrust-time predictability is important. This change is believed to be the result of liquid  $N_2H_4$  initially penetrating deeply into the bed; then, as the entire reactor warms, a part of

this liquid region reaches a temperature such that the liquid vaporizes, decomposes, and changes the temperature distribution, establishing a new equilibrium condition. The entire process requires only a few milliseconds.

Once the second steady state is established, it will persist as long as the reactor is in operation. This *spiking* is one of the difficulties discovered when Shell 405 was used in a reactor that operated very satisfactorily with the nonspontaneous catalyst.

Again, this problem can be alleviated by a layer of granular catalyst at the top of the bed. This layer apparently provides enough surface area so that the incoming hydrazine is completely vaporized and the decomposition process firmly established in the first 0.1–0.2 in. of the bed during the initial start transient.

*c. Loss of catalytic activity.* Loss of catalytic activity could conceivably result from any of several causes. Some of these causes are: decrease of the total catalyst surface area, crystalline growth of the active metal, poisoning of the catalyst, and physical loss of catalyst. Poisoning is not a problem with neat hydrazine, but can occur from free carbon or sulfur. Attempts at promoting the catalytic decomposition of mixed hydrazine fuels (added MMH or UDMH) have been almost totally unsuccessful because of the presence of carbon.

The surface area loss and active metal recrystallization are known to occur, but, as was noted in Ref. 21, the only observed effect has been a longer ignition delay for subsequent cold bed starts, particularly when the bed is near the freezing temperature of hydrazine. One of the difficulties is the lack of a sensitive, quantitative, and definitive measurement of catalyst activity. Ignition delay can be used, but it is too heavily dependent on the reactor design to be very useful.

*d. Physical loss of catalyst.* By far the most serious problem is the physical loss of catalyst that can result in very rough operation. This loss is the result of relative motion of adjacent catalyst particles with the subsequent abrasion of the particles and the crushing of individual pellets from pressure drop loads. The net result is the generation of *fines*, which are loosely defined as particles smaller than 1/3 the size of the smallest particles originally loaded into the reactor. These *fines* can easily pass between the larger particles; many pass completely out of the reaction chamber.

The problem of *fines* is far from being completely solved. The origin can be from at least two sources: mechanically induced vibration, such as from a launch vehicle environment, and abrasion during operation. Unequal thermal expansion of the catalyst and the reactor results in an apparent decrease in bed volume during reactor operation, and further loosens the catalyst, accentuating the abrading process. The top of the bed is particularly susceptible to the unequal thermal expansion. An obvious approach is to hold the catalyst securely in place. Spring loaded devices have been tried with some success. A NASA-funded investigation is just beginning to explore the possibility of deliberately fusing the individual particles together (Contract NAS 7-583, Rocket Research Corp.). If this fusing can be accomplished without adversely affecting other bed properties, it could be very successful. The Shell Development Co., under an Air Force contract, is attempting to develop carriers with improved high temperature properties.

The rates at which catalyst is lost have been measured for many reactors. However, it is meaningless to list these rates without also giving details of the reactor, the operating conditions, prior history of the catalyst, etc. Two examples will be cited, however, to illustrate the magnitude of the problem. During the course of the work described in Ref. 25, widely varying loss rates were noted. Amounts as high as 10% of the original amount of catalyst loaded were lost per minute. Shortly after this, an improved carrier was found for the granular catalyst, reducing the loss rate by nearly an order of magnitude. More recently, one concern operated a 0.1-lbf thrust reactor continuously for 3.5 h. During that period, 10% of the original catalyst was lost, representing a rate of just slightly under 0.05%/min.

## B. Performance of Continuously Operated Devices

Theoretical performance of these devices has already been presented in Figs. 2 and 3. Always a crucial criterion in the rocket engine industry is the fraction of the theoretical performance that can be attained. Since mixing and atomization are not key requirements, 95–98% of the theoretical vacuum specific impulse  $I_{sp\ vac}$ , shown in Fig. 3, is commonly achieved over a wide range of operating conditions. Small size reactors may not do as well because of higher heat losses through the reactor walls. Reactors that operate at a high bed loading may likewise suffer because of channeling. Nevertheless, it is not unreasonable to expect to achieve 95% of theoretical  $I_{sp\ vac}$ .

A separate criterion is the absolute level of performance that can be expected or the fraction of dissociated ammonia that can be achieved. Reference 25 reported a minimum value of about 55% of the ammonia was dissociated for the Shell 405 catalyst, the limitation being a bed length long enough to achieve an acceptable level of roughness. A random variation in chamber pressure of  $\pm 4\%$  was used as the criterion. A reactor (see Fig. 12) using a nonspontaneous catalyst operates at an ammonia dissociation level between 50 and 55%. The measured  $I_{sp\ vac}$ , at  $\epsilon = 44:1$  for this reactor, is 235 lbf-s/lbm and represents approximately 97% of theoretical performance.

In general, reactors that use the Shell 405 will produce more dissociated ammonia than those packed with a nonspontaneous catalyst, because of the greater activity of the former type catalyst. Thus, reactors using Shell 405 and designed according to the criteria of Ref. 25 can be expected to yield slightly less performance (about 5 lbf-s/lbm in specific impulse).

However, some recent developmental work shows promise in reducing this performance differential. Several reactors have been tested with beds shorter than those recommended by Ref. 25. A second advance is the successful use of higher bed loadings than those covered by Ref. 25. Values of  $G$  (propellant flow rate/cross-sectional area of catalyst bed) as high as 0.08 lbm/in.<sup>2</sup>-s have been reported. Both of these advances are possible primarily because of improved catalyst retention techniques.

A third improvement being developed is the use of beds composed of a mixture of spontaneous and nonspontaneous catalyst. The reactor (see Fig. 14) as described in a later section uses this type of bed. Not only is the ammonia dissociation reduced, but this reactor runs smoother and the catalyst costs are reduced. Some investigators have reported success in using layered beds composed largely of nonspontaneous catalyst below a thin layer of Shell 405.

The performance of continuously operated reactors can be summarized as follows. A reactor can be built for most applications to deliver a minimum of 95% of theoretical vacuum specific impulse. The use of a nonspontaneous catalyst will result in less ammonia dissociated than the use of the Shell 405. However, this difference will most likely be reduced in the near future. In any case, delivered specific impulses of 230–235 lbf-s/lbm,

for an expansion area ratio of 50:1, are realized easily within the present state of the art.

### C. Intermittently Operated Thrust Producing Devices

Development of the Shell 405 catalyst has perhaps its greatest impact in the area of intermittently operated (i.e., pulsed) devices, because of the capability of making repeated cold bed starts. Since repeated starts with nonspontaneous catalysts is possible only if the bed is hot, hydrazine did not receive serious consideration for pulse use until the advent of the Shell 405. Pulse operation is characterized by very short periods of propellant flow to the reaction chamber, as well as by many starts and stops of the reactor operation.

Potential applications are for attitude control devices, maintaining a satellite in a prescribed orbit, etc. These kinds of applications can require widely varying on-times (i.e., the time during which the reactor is operating), as well as various duty cycles (i.e., the on-time fraction of a complete on-off cycle).

Because of the extensive backlog of experience with nonspontaneous catalysts, converting from nonspontaneous catalysts to the Shell 405 for continuously operated reactors was relatively straightforward. Such was not the case for pulsed reactors. Thus, this entire field is less extensively explored than the continuously operated reactors, but it is being actively pursued by industry. Parts of the information needed to characterize pulse-mode reactors have been gathered by individual companies, but as yet there has not been a report in the open literature of a systematic program directed at this technology area.

Pulse operation of a hydrazine monopropellant reactor creates a set of problems not encountered during steady-state operation. Very short start and shutdown transients are generally required over a varying range of environmental conditions. Reproducibility is often more important than a short pulse requirement, especially reproducibility of the impulse centroid. One common approach to shortening the start transient is to increase the bed loading. But this approach can drastically affect the catalyst loss rate. Repeated pulses also appear to be more detrimental to the catalyst than continuous operation.

*1. Start transient.* The start transient is usually described in terms of the time from the propellant-valve electrical-on signal until 90% of the final steady-state, or

rated, thrust is reached. Included in this overall response time are:

- (1) The valve opening time.
- (2) The time to fill the propellant feed system.
- (3) The time between introduction of hydrazine to the catalyst bed and the beginning of the decomposition reaction (i.e., the ignition delay).
- (4) The time required to generate enough gas to raise the chamber pressure to near its final value.

The valve actuation and feed system fill times can, of course, be reduced by proper design. The ignition delay and the rise time are strongly affected by the injection scheme, the catalyst bed geometry, the history of the catalyst, and the initial catalyst and propellant temperatures.

Whatever the application, injectors generally receive a great amount of attention. This is primarily the result of injector design being largely a "black art," even for a system as simple as monopropellant hydrazine. It would appear that every group that works with hydrazine develops a favorite injection scheme which each feels has advantages over any other. Usually these techniques are considered proprietary and will not be described in any detail here. In general, the objective of these different injectors for pulsed applications is to contact as much catalyst in as short a time as possible. This goal can lead to an injector that does not inject all or even most of the hydrazine in an axial direction. It can also lead to high G-loading approaches. The majority of these different schemes achieve a total response time on the order of 10–20 ms for a warm catalyst bed, and several can approach this time for an initial bed temperature of less than 100°F.

The catalyst bed geometry for pulsed reactors is dominated by the need to place a maximum catalyst surface area adjacent to the injector. This requirement presents no problem for low-thrust devices since a small-sized granular catalyst is required anyway. For some larger reactors, the bed is composed of two sizes of catalyst particles to reduce the pressure drop. The small catalyst is placed nearest the injector. Many different geometric approaches to this problem have been tried; most reasonable ones appear to work satisfactorily.

As was noted in the description of steady-state thrusters, the internal surface area of the catalyst can change significantly depending on the history of the catalyst. The

principal factor seems to be high temperature, since the same result can be obtained in an oven and the principal result is a decrease in surface area (see Fig. 1). For a duty cycle where the bed temperature remains above approximately 300°F, this surface area change presents no difficulty. However, there are applications where the bed will cool well below 300°F between periods of operation. As noted in Ref. 21, this low temperature is precisely the condition for which surface area change is important and will significantly affect the start transient. It would be very desirable to control the effect of surface area on cold bed starts, but, most likely, only how to predict the effect will be known.

The initial temperatures of the catalyst bed and the propellant have a very strong influence on the start transient and the shape of the entire pulse. A preliminary investigation of this effect is included in Ref. 21. Figure 6 shows the effect of bed temperature on ignition delay. Figure 7 illustrates the effect of bed temperature on the pulse shape. The experiment that Fig. 7 illustrates consisted of firing a reactor for 10 pulses (60 ms on and 340

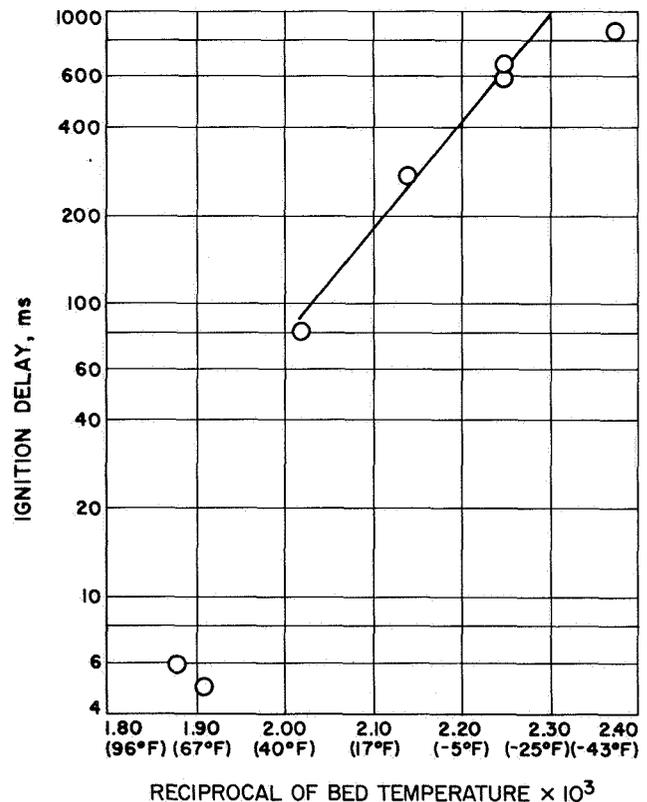


Fig. 6. Ignition delay vs the reciprocal of bed temperature (reprinted from Ref. 21)

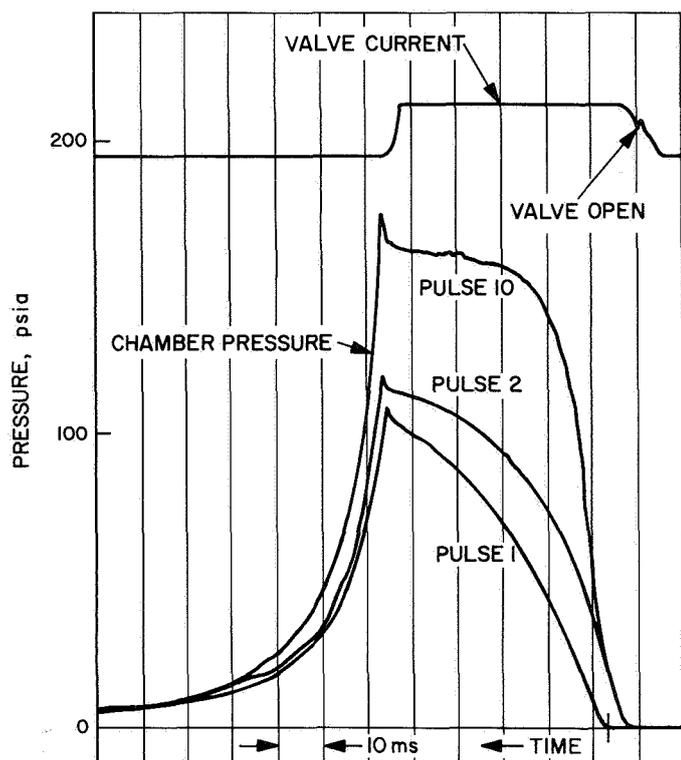


Fig. 7. Characteristic reactor response vs chamber pressure (reprinted from Ref. 21)

ms off), followed by 10 s of continuous operation, and then another 10 pulses. In contrast to the results shown in Fig. 7, the 10 pulses after the continuous operation are nearly identical in both the start transient and the pulse shape.

It would appear, from the evidence to date, that building a reactor producing identical pulse shapes for different combinations of initial bed and propellant temperatures and catalyst histories is not likely in the near future. It is much more likely that the ability to predict the effect of these variables accurately will be achieved.

For applications where a long series of pulses are required, the error from the nonreproducibility introduced by the first several pulses becomes negligible. In recognition of the difficulties involved in making all pulses in a series match later pulses, the reproducibility requirement is often written in terms of a later pulse. Often the sixth pulse is used. This requirement is similar to that encountered with hydrogen peroxide reactors.

**2. Catalyst bed lifetime.** As was the case for continuously operated reactors, the physical loss of catalyst can be a problem for pulsed reactors. However, the problem does appear more severe for pulsing. Apparently, many periods of short operations impose a more severe environment than an equivalent amount of continuous operation.

Several companies have built reactors capable of several hundred thousand pulses with a total on-time on the order of 50,000 s (14 h). These reactors generally operate at a low bed loading.

High bed loading is certainly a more stringent condition. A long train of pulses is a much less difficult requirement than many starts with a *cold* bed, a condition most likely to be affected by catalyst degradation.

To summarize, it is possible to achieve long lifetimes for pulsed reactors. Long-life requirements and severe operating conditions require careful design and the use of more sophisticated catalyst retention techniques.

**3. Heat transfer to the propellant feed system.** Any system that uses hydrazine must be designed so as to severely limit the amount of heat conducted to any region where the fluid is stagnated. The consequences of not observing this rule are generally disastrous, since the hydrazine will surely decompose with the release of large quantities of gas and energy. This fact has been demonstrated many times in both monopropellant and bipropellant rocket engines. Balancing this tendency of hydrazine to decompose is the fact that it is a relatively good coolant and can absorb fairly large quantities of energy before vaporizing and decomposing.

Since monopropellant hydrazine reactors normally operate without any cooling, the metallic chamber can easily reach a temperature of 1700–2000°F. Heat from the chamber can be conducted into the propellant feed system. This conduction presents no great problem when the reactor is operated continuously, since, unless there has been a gross design error, the flowing hydrazine can easily absorb this energy. With pulsed reactors, this heat transfer problem is not easily avoided. During periods of no propellant flow it is quite possible to transfer enough heat to the upstream side of the propellant valve to locally decompose the hydrazine. Even the injector may become hot enough to decompose the hydrazine there. Figure 8 shows typical injector temperatures that a properly designed reactor may reach.

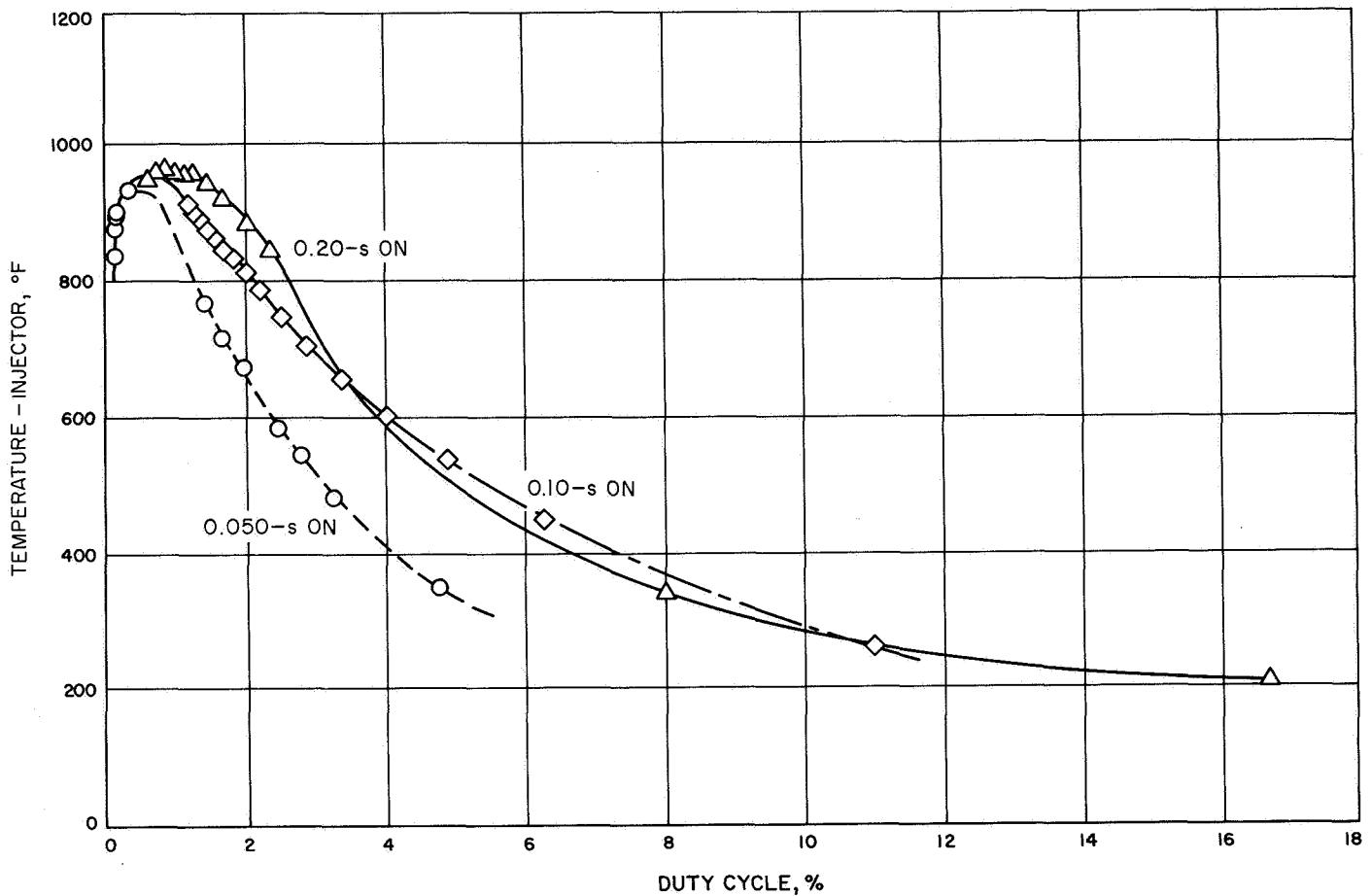


Fig. 8. Injector head temperature as a function of duty cycle (reprinted by permission of Rocket Research Corp.)

The solution is to thermally isolate the critical parts of the liquid system from the chamber and catalyst bed, and to make sure that there are no parts of the feed system where hydrazine is heated while stagnant. The most common technique used is to make the conduction path as long and thin as possible to introduce a large thermal resistance. Often a long capillary tube (or tubes) connects the propellant valve to the injector, and the valve is mounted on a thin-walled structural member. This technique has the disadvantage of increasing the system liquid volume and, hence, the transient times. Seal materials having very low thermal conductivities are often used, thus doing double duty as an insulator as well.

The problem of heat conduction to the feed system is one that can be handled by proper design. Each reactor must be treated according to its intended use. The duty cycle and on-time must be considered, as well as the external environment. The use of computer programs for solutions to transient heat transfer problems has proved to be an important tool to this end.

#### D. Performance of Intermittently Operated Thrust Producing Devices

Pulsed operation of a reactor may result in less of the potentially available chemical energy being converted to sensible heat during a single pulse than for an equivalent period of continuous operation. This energy loss is the result of a significant part of the released chemical energy being lost first to heat the catalyst particles and chamber walls, and then to the external environment by convection and radiation. This effect is illustrated in Fig. 9 which shows vacuum specific impulse vs the on-time for a specified duty cycle. The shorter the pulse and the longer the time between pulses, the lower the impulse.

Also, Fig. 9 shows the impulse after the reactor has reached steady-state following a series of pulses that bring the reactor to some equilibrium temperature with its surroundings. Another illustration of this effect is shown in Fig. 10, where vacuum specific impulse is plotted vs the pulse number (in a series) for a given duty cycle and various values of on time.

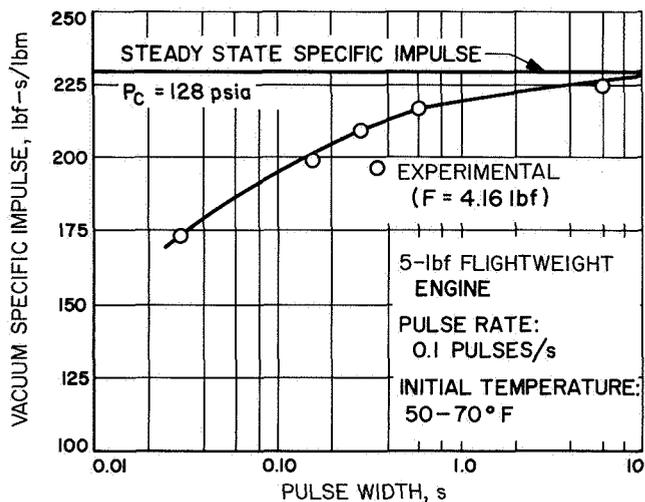


Fig. 9. Effect of pulse width on specific impulse (reprinted by permission of Hamilton Standard Div. of United Aircraft Corp.)

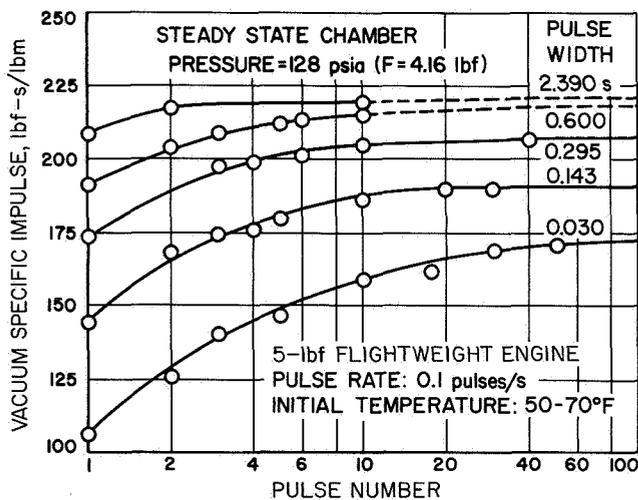


Fig. 10. Effect of pulse number and pulse width on specific impulse (reprinted by permission of Hamilton Standard Div. of United Aircraft Corp.)

### E. Gas Generators

Monopropellant hydrazine is ideally suited for gas generation. A hydrazine gas generator differs from a reactor, which produces thrust, only in the use made of the decomposition products. The major goal for any gas generator is to produce a large volume of cool, clean gas that will not condense. Hydrazine and catalytic decomposition chambers meet these requirements extremely well. If 75% of ammonia is decomposed, each lbm of liquid

hydrazine will produce about 30 ft<sup>3</sup> of gas at standard temperature and pressure.

The gas generator problems are the same as those already noted for thrusters. In fact, almost any thruster could also serve as a gas generator. The gas generator would differ only by the absence of an expansion nozzle and by the catalyst bed being slightly longer to promote ammonia dissociation, thus lowering the molecular weight and gas temperature and increasing the volume of gas produced.

An application of a monopropellant hydrazine gas generator is described in Ref. 9. This gas generator employed a nonspontaneous catalyst and was equivalent to a thruster producing about 20 lbf. This generator fulfilled all the design requirements and was capable of pumping 11 lbm/s of liquid propellants. Another gas generator built and tested at JPL to drive the Jupiter turbopumps was equivalent to a 1000-lbf thrust rocket. Current work at Rocket Research Corp. under Hercules subcontract involves a large-throttled gas generator.

Some of the more interesting applications of hydrazine and hydrazine mixtures are being made with gas generators. The Naval Ordnance Test Station at China Lake, Calif., has been especially active in this field. The Navy is interested in the deep-ocean recovery of objects, and has successfully applied monopropellant hydrazine to this problem. By expelling the gases from a reactor into a rubber buoyancy bag, the Navy has made free-ascent-lifts of 4000 lbm from a depth of 2800 ft. Another successful test has been a lift of 53,000 lbm from a depth of 85 ft (Ref. 27). As a prelude to work at even greater depths, the Navy has operated reactors at chamber pressures as high as 11,500 psi. These latter tests were conducted at sea level.

Other applications currently under development will only be mentioned to show the variety of uses possible. A large-throttled hydrazine gas generator is being used to supply the gas for a mass-excited solid-propellant rocket (Rocket Research Corp. under Hercules subcontract). Turbo-alternator systems for the generation of electrical power are being developed using hydrazine as the energy source. Attitude control systems that combine the advantages of cold gas thrusters with the compactness of monopropellant hydrazine have been tested (Ref. 28). The gas generator products are stored in a plenum which then supplies cold gas on demand. These are only a few of the many applications of hydrazine gas generators.

## V. Monopropellant Hydrazine Thruster Use on Flight Systems

### A. Ranger-Mariner

In the past, 50-lbf thrust, nonspontaneous catalyst reactors were employed on the JPL *Ranger* and *Mariner* spacecraft for trajectory correction maneuvers (Refs. 29-31). These rocket engines used a 15-cm<sup>3</sup> start slug of nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>) for ignition and initial catalyst bed heating. A schematic diagram of the *Mariner-C* propulsion system is shown in Fig. 11. This system was used for both *Mariner IV*, now in solar orbit, and *Mariner V*, the successful Venus probe. The use of dual explosively-actuated valves and oxidizer start cart-

ridges provided the capability of two separate course corrections.

A cross-section view of the Haynes Alloy No. 25 reactor assembly is shown in Fig. 12. The injector consists of five swirl-type atomizers, four for fuel and one for oxidizer, the latter one being employed only during the first second of operation. The catalyst bed consists of JPL Type H-7 spherical particles (3/16-in. diameter).

During qualification, this engine was subjected to:

- (1) Humidity testing consisting of a soak at 21°C and 95% humidity, followed by exposure to 38°C and 95% humidity for 30 min.

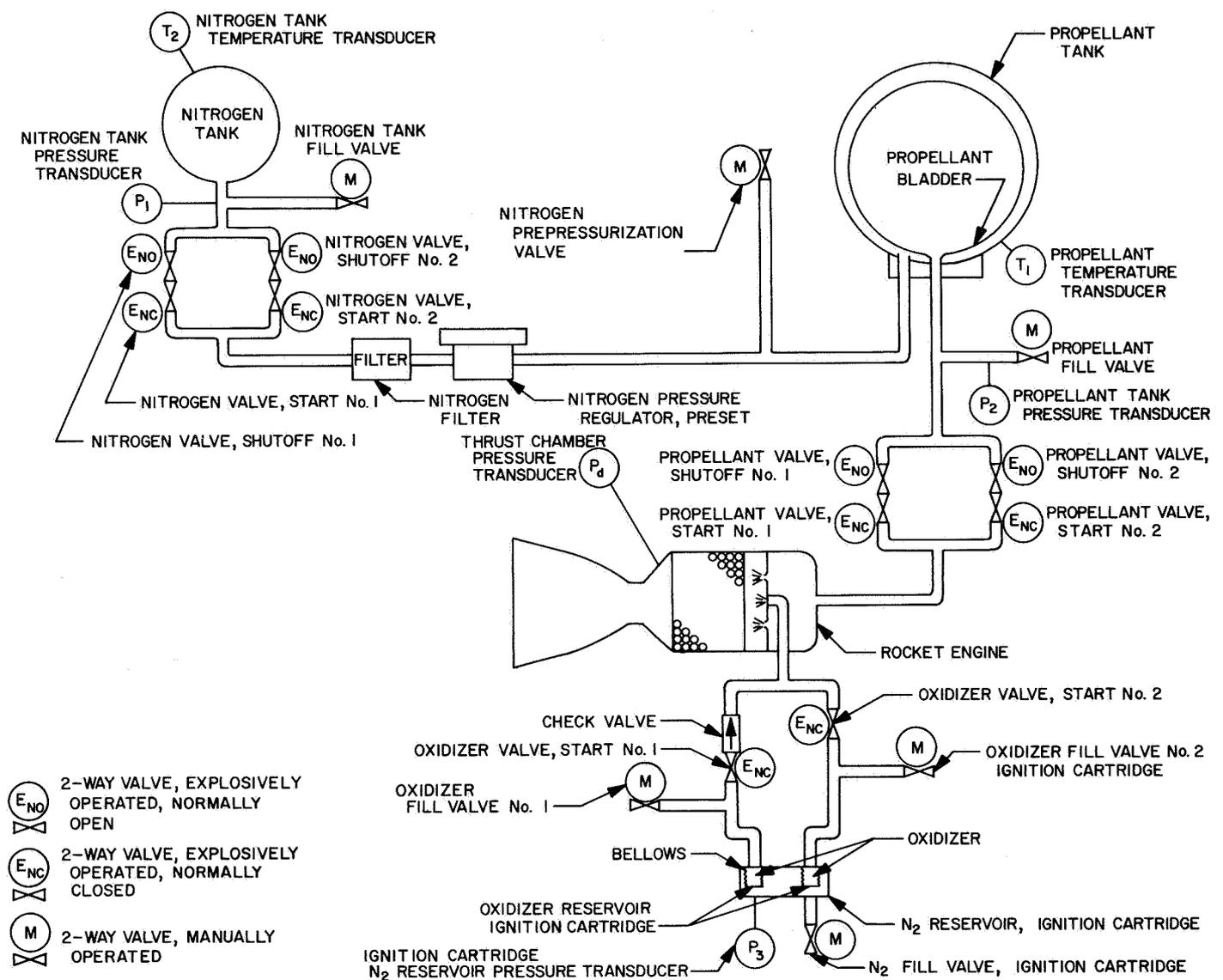
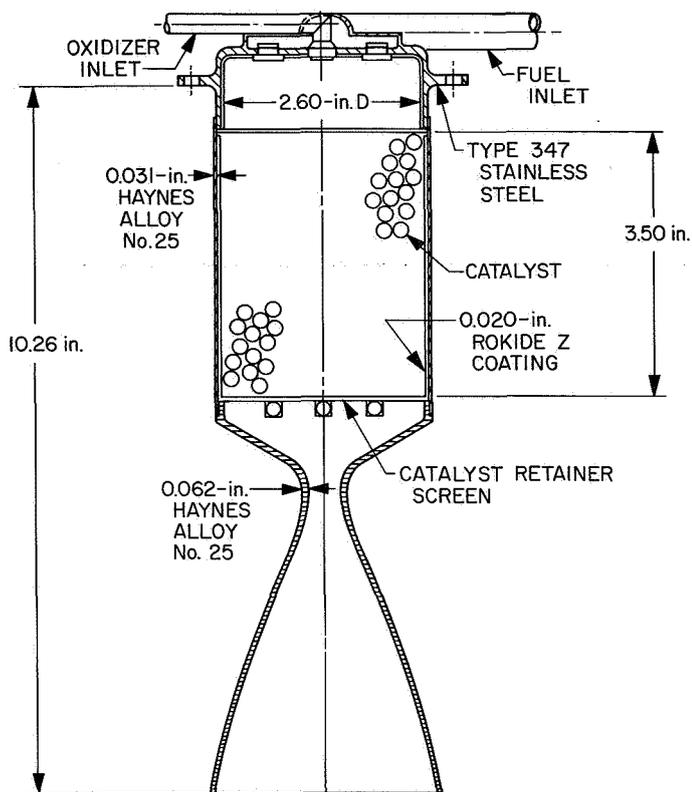


Fig. 11. *Mariner C* post-injection propulsion system schematic



**Fig. 12. Ranger-Mariner monopropellant hydrazine 50-lbf thrust rocket engine (nonspontaneous catalyst)**

- (2) A shock test of 100 g, 0.5- to 1.5-ms duration, five times in each of three orthogonal directions.
- (3) Static acceleration of 14 g in three orthogonal directions for 5 min each.
- (4) Low frequency vibration of 3-g peak from 4.4 to 15 Hz followed by complex wave vibration consisting of 14-g-RMS noise for 36 s, and a total of 600 s of 5-g-RMS noise, 2-g-RMS sinusoid, and 9-g-RMS sinusoid.

For margin limit purposes, the engine was then test fired for 200 s during two separate tests, both tests at a chamber pressure that was 1.25 times the normal operating pressure (normal run duration and pressure are 100 s and 190 psia, respectively). Two tests, each of 100-s duration, were conducted with the engine installed in an inverted position. The purpose of these tests was to demonstrate that, after shutdown, the propellant contained within the injector will vaporize without undergoing explosive decomposition as a result of heat soak back into the injector from the hot catalyst bed. All of these tests were successful.

The most significant problem encountered was the generation of catalyst *fines* during vibration. These *fines* consisted of a relatively small quantity (a gram or less) of metal impregnated aluminum oxide with individual particle sizes ranging from those of dust to those of coarse sand (1-500  $\mu\text{m}$ ). Although the loss of these particles has no measurable effect on the reactor performance, their presence is potentially detrimental to sensitive optical instruments. During the *Ranger* and *Mariner* programs, an analysis was performed which indicated that the solar pressure would effectively blow away these particles within a matter of hours. No problems have ever been identified that could have been caused by these catalyst *fines*, nevertheless, their presence cannot be ignored. An obvious solution to contain them within the reactor until it is fired would be to use a frangible diaphragm to close the nozzle. Similar devices are used on solid propellant rockets.

Perhaps our best space storage data on hydrazine systems is being obtained from *Mariner IV*, launched during Nov. 1964. Although its primary mission of obtaining Mars scientific data has been completed, *Mariner IV* is still a fully operational spacecraft and data is obtained about once weekly at this time.

The *Mariner* system uses a butyl bladder within a titanium propellant tank. This propellant containment scheme has been quite effective. Since the propellant tank is isolated from the high pressure nitrogen source by an explosive valve assembly, any gas formation resulting from the propellant either reacting with the bladder, or undergoing homogeneous or heterogeneous decomposition, would result in a propellant tank pressure increase.

A plot of propellant tank pressure increase due to decomposition is shown in Fig. 13. The data have been corrected for pressure changes resulting from temperature effects. A moderate ( $\sim 70$  psi) pressure increase has occurred over a 2½-yr period. Also, the propellant temperature has been quite moderate (46-67°F).

Extrapolation of the Eberstein and Glassman rate constants (Ref. 23) to these temperatures reveals that noticeable gas phase homogeneous decomposition should not be expected over a 3-yr period. Thus, the observed pressure rise is concluded to be only due to reaction with the bladder material or to heterogeneous decomposition, catalyzed either by the bladder or, more unlikely, by the titanium tank walls.

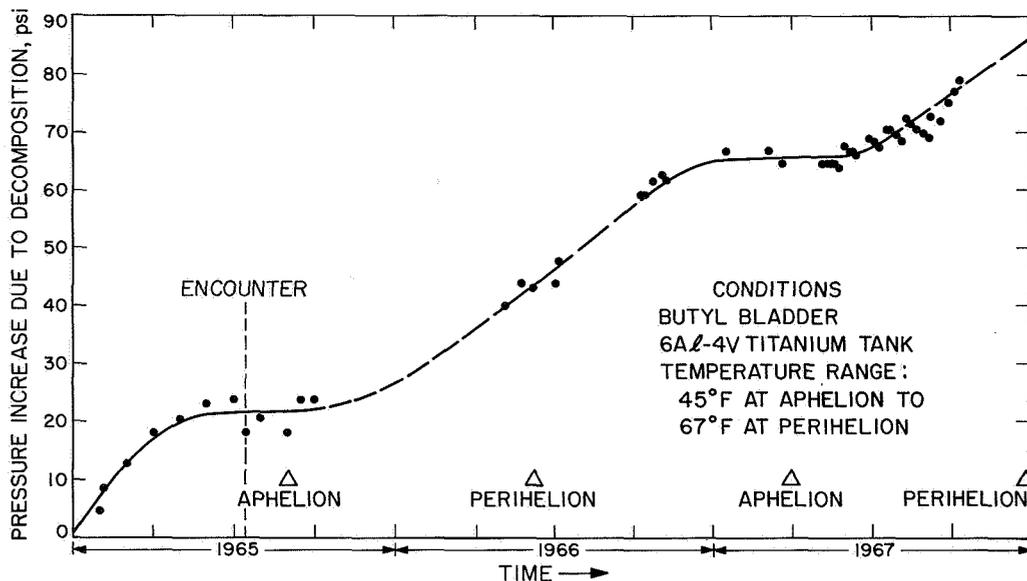


Fig. 13. Mariner IV fuel tank pressure increase as a function of flight time

Higher temperatures, especially those in excess of 100°F, are more detrimental because of marginal compatibility with the butyl bladder (Ref. 31). A second burn of the propulsion subsystem was accomplished in October of 1967. This successful operation conclusively established the space storability of the nonspontaneous catalyst.

#### B. Mariner 1969

For the Mariner 1969 mission to Mars, JPL has elected to fly a spontaneous catalyst engine in lieu of the previous nonspontaneous types. Although multiple operation is not a requirement (only two starts are required), the inherently simpler system and increased reliability were overpowering reasons to upgrade the system.

A cutaway of this 50-lbf thrust reactor is shown in Fig. 14. A showerhead type injector is used and 20-mesh Shell 405 catalyst is packed directly against a 60-mesh screen that is adjacent to the injector face. The remainder of the catalyst bed consists of a mixture of 75% Shell 405 1/8-in. cylindrical particles and 25% JPL Type H-A-3 1/8-in. cylindrical particles. The Type H-A-3 nonspontaneous catalyst was added after tests showed that it promoted smoother reactor operation. Roughness values, based on chamber pressure excursions, now run about  $\pm 2\%$ , equivalent to those values obtained on the previous Mariner nonspontaneous catalyst engines.

This engine has undergone a prequalification test series similar to that described previously. It appears to be an

equivalent reactor but for two exceptions. First, the quantity of catalyst fines generated during vibration appears to be somewhat greater; and second, this reactor appears to degrade faster as run time is accumulated. This degradation takes the form of rougher operation. For example, the Mariner 1969 prequalification engine roughness, after all environmental tests, was  $\pm 4\%$  at the end of 330-s accumulated time (individual tests of 30, 100, and 200 s).

#### C. Intelsat

TRW Systems is currently fabricating 3.5-lbf thrusters and the associated feed system for Intelsat-3. These reactors are capable of either pulsed or continuous operation. A complete description of this system is contained in Ref. 32.

#### D. Transtage

Rocket Research Corp. is developing 25-lbf thrust engines under Martin-Denver subcontract for the Transtage vehicle. The significant point with regard to this work is that this monopropellant system will replace an existing bipropellant system to gain higher reliability.

#### E. ATS-C

Hamilton-Standard is delivering 5-lbf thrust reactors to Hughes Aircraft for use on the ATS-C satellite. Previously, two redundant peroxide systems have been used; now, one of these systems will use hydrazine.

## F. NRL Satellite

Rocket Research Corp. has delivered a 0.5-lbf system to the Naval Research Laboratory for use in one of their small research satellites.

These programs summarize most of the known unclassified flight project usage of hydrazine systems. There are many other applications now being studied. One of the more interesting of these is for the *Voyager* capsule descent propulsion system. Although a relatively high thrust is required (up to 2000 lbf total), the moderate total impulse requirement, together with the possible use of multiple engine configurations, make the use of monopropellant hydrazine feasible for this purpose. The recent success at JPL in heat sterilizing a simple Shell 405 system (275°F, 6 cycles), using a non-bladdered titanium *Ranger* tank (Ref. 33), has demonstrated the feasibility of heat sterilizing these systems.

## VI. Conclusion

Monopropellant hydrazine is a rapidly expanding technology area. Only now does it appear that the full potential is about to be realized. The development of the spontaneous Shell 405 catalyst has greatly expanded the interest in the very simple monopropellant hydrazine systems. The capability of many spontaneous ignitions and the system simplicity possible with the Shell 405 are the primary reasons for this growing interest.

A monopropellant hydrazine reactor has flown on each of the JPL *Ranger* and *Mariner* spacecraft and, in the

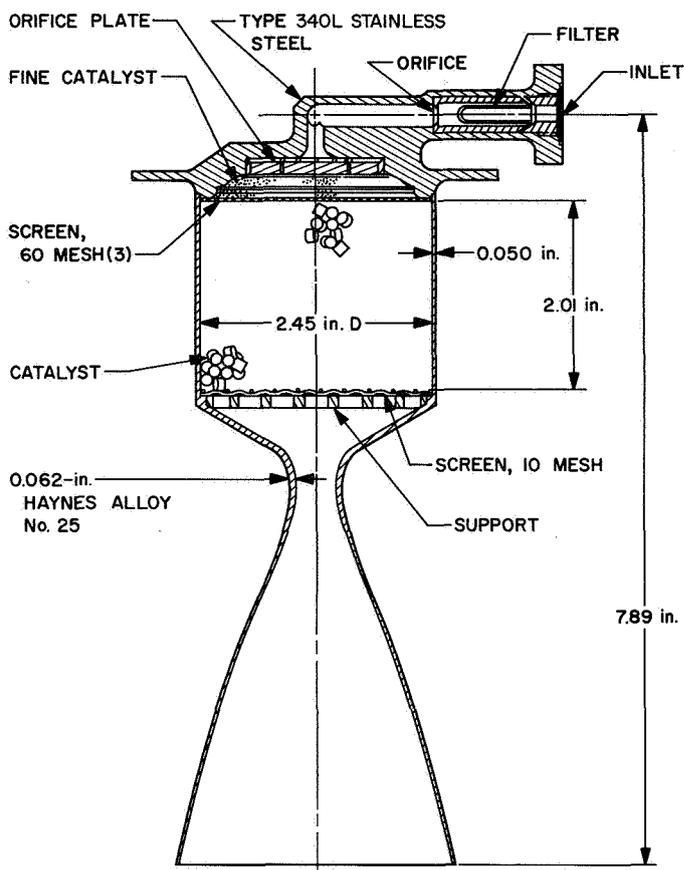


Fig. 14. *Mariner* 1969 spontaneous catalyst 50-lbf thrust rocket engine

very near future, reactors using the Shell 405 catalyst will be an important part of several vehicles. The next few years should see many more applications.

## References

1. Altman, D., and Thomas, D. D., *Evaluation of Hydrazine as a Monopropellant and Gas Generant*, Progress Report 9-36. Jet Propulsion Laboratory, Pasadena, Calif., Apr. 1949.
2. Thomas, D. D., *The Thermal Decomposition of Hydrazine*, Progress Report 9-14. Jet Propulsion Laboratory, Pasadena, Calif., Aug. 1947.
3. Grant, A. F., Jr., *Catalysts for the Thermal Decomposition of Hydrazine When Used as a Monopropellant or as a Gas Generant*, Publication 15. Jet Propulsion Laboratory, Pasadena, Calif., Feb. 1953.
4. Grant, A. F., Jr., *Development of Hydrazine as a Monopropellant and Gas Generant*, Report 9-1. Jet Propulsion Laboratory, Pasadena, Calif. Mar. 1950.
5. Grant, A. F., Jr., *Basic Factors Involved in the Design and Operation of Catalytic Monopropellant-Hydrazine Reaction Chambers*, Report 20-77. Jet Propulsion Laboratory, Pasadena, Calif., Dec. 1954.
6. Evans, D. D., and Lee, D. H., *Ignition Means for Monopropellant*, U.S. Patent 3,298,182 (issued to J. E. Webb, NASA). U.S. Department of Commerce, Washington, June 1964.
7. Lee, D. H., and Foster, C. R., *A Monopropellant-Hydrazine Turboalternator Auxiliary Power Unit*, Publication 81, Jet Propulsion Laboratory, Pasadena, Calif., Jan. 1957 (Confidential).
8. Foster, C. R., Gorden, E., and Van de Verg, N., *Experimental Liquid-Propellant Gun Firings at the Jet Propulsion Laboratory*, Publication 29. Jet Propulsion Laboratory, Pasadena, Calif., Mar. 1954.
9. Lee, D. H., and Evans, D. D., *The Development of a Heated-Hybrid Generated Gas Pressurization System for Propellant Tanks*, Technical Report 32-375. Jet Propulsion Laboratory, Pasadena, Calif., Feb. 1963.
10. Audrith, L. F., and Ogg, B. A., *The Chemistry of Hydrazine*. John Wiley and Sons, Inc., New York, 1951.
11. Thomas, D. D., *Liquid-Vapor-Solid Equilibria for Ammonia-Hydrazine System*, Memorandum 9-12. Jet Propulsion Laboratory, Pasadena, Calif., Apr. 1948.
12. Elverum, G. W., Jr., and Cole, L. G., *Some Physical-Chemical Studies of Hydrazine-Hydrazine Nitrate-Water*, Memorandum 20-79. Jet Propulsion Laboratory, Pasadena, Calif., Dec. 1952.
13. Petker, I., Wilford, D. B., and Mason, D. M., *A Study of Some Freezing Point Depressants for Hydrazine and Their Properties*, Progress Report 20-238. Jet Propulsion Laboratory, Pasadena, Calif., Nov. 1954.
14. Vango, S. P., and Krasinsky, J. B., *Density, Vapor Pressure, and Viscosity of Solutions of Hydrazine Mononitrate in Hydrazine*, Technical Memorandum 33-103. Jet Propulsion Laboratory, Pasadena, Calif., Oct. 1962.

## References (contd)

15. Vango, S. P., and Krasinsky, J. B., *Hydrazine Mononitrate in Hydrazine, Supplemental Physical Data*, Technical Memorandum 33-122. Jet Propulsion Laboratory, Pasadena, Calif., Mar. 1963.
16. Lee, D. H., *A Survey of the Compatibility of Various Materials with Hydrazine and Mixtures of Hydrazine, Hydrazine Nitrate, and Water*, Memorandum 20-152. Jet Propulsion Laboratory, Pasadena, Calif., 1957.
17. Toth, L. R., "Material Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-44, Vol. IV, p. 175. Jet Propulsion Laboratory, Pasadena, Calif., Apr. 1967.
18. Hollywood, L. P., Metz, T. R., and Porter, R. N., *Storage Tests of Nitrogen Tetroxide and Hydrazine in Aluminum Containers*, Technical Report 32-1039. Jet Propulsion Laboratory, Pasadena, Calif., Jan. 1967.
19. Stanford, H. B., "Hydrazine Sterilization Tests," in *Supporting Research and Advanced Development*, Space Programs Summary 37-35, Vol. IV, p. 155. Jet Propulsion Laboratory, Pasadena, Calif., Oct. 1965.
20. Voge, H. H., et al., *Development of Catalysts for Monopropellant Decomposition of Hydrazine*, Final Report 3-13947, Contract NAS 7-97. Shell Development Company, Emeryville, Calif., Apr.-Dec. 1964 (Confidential).
21. Carlson, R. A., and Baker, W., *Space Environmental Operation of Experimental Hydrazine Reactors*, Final Report 4712, Contract NAS 7-520. TRW Systems Group, Redondo Beach, Calif., Apr. 1967.
22. McHale, E. T., Knox, B. E., and Palmer, H. B., "Determination of the Decomposition Kinetics of Hydrazine Using a Single-Pulse Shock Tube," in *Tenth Symposium (International) on Combustion, University of Cambridge, Cambridge, England, Aug. 17-21, 1964*. Combustion Institute, Pittsburg, Pa., 1965.
23. Eberstein, I. J., and Glassman, I., "The Gas-Phase Decomposition of Hydrazine and its Methyl Derivatives," in *Tenth Symposium (International) on Combustion, University of Cambridge, Cambridge, England, Aug. 17-21, 1964*. Combustion Institute, Pittsburgh, Pa., 1965.
24. Lee, D. H., *Performance Calculations for Monopropellant Hydrazine and Monopropellant Hydrazine-Hydrazine Nitrate Mixtures*, Technical Report 32-348. Jet Propulsion Laboratory, Pasadena, Calif., Dec. 1962.
25. *Development of Design and Scaling Criteria for Monopropellant Hydrazine Reactors Employing Shell 405 Spontaneous Catalyst*, Final Report RRC-66-R-76 Volumes I and II, Contract NAS 7-372, Rocket Research Corp., Seattle, Wash., Jan. 1967.
26. Kesten, A. S., *Analytical Study of Catalytic Reactors for Hydrazine Decomposition—First Annual Report*, UACRL F910461-12, Contract NAS 7-458. Research Laboratories, United Aircraft Corp., East Hartford, Conn., May 1967.

## References (contd)

27. Witcher, J., and Miller, D., "Recovery of Deep-Ocean Objects Using Hydrazine-Powered Buoyancy Devices," paper to be presented at the Monopropellant Technology Symposium, Johns Hopkins University, Silver Spring, Md., Nov. 28-30, 1967.
28. Groudle, T. A., "Reaction Control Gas Supply System," in *Supporting Research and Advanced Development*, Space Programs Summary 37-44, Vol. IV, p. 171. Jet Propulsion Laboratory, Pasadena, Calif., Apr. 1967.
29. Lee, D. H., *Development of the Midcourse Trajectory-Correction Propulsion System for the Ranger Spacecraft*, Technical Report 32-335. Jet Propulsion Laboratory, Pasadena, Calif., Mar. 1963.
30. Evans, D. D., Groudle, T. A., and Mattson, R. F., *Development of the Ranger Block III Spacecraft Propulsion System*, Technical Report 32-829. Jet Propulsion Laboratory, Pasadena, Calif., Mar. 1966.
31. Schmitz, B. W., Groudle, T. A., and Kelley, J. H., *Development of the Post-injection Propulsion System for the Mariner-C Spacecraft*, Technical Report 32-830. Jet Propulsion Laboratory, Pasadena, Calif., Apr. 1966.
32. Mosley, V., et al., "Development of the Monopropellant-Hydrazine Propulsion System for *Intelsat-3*," Paper L67-60 in *Proceedings of the Ninth Liquid Propulsion Symposium*, St. Louis, Mo., Oct. 25-27, 1967, sponsored by the Interagency Chemical Rocket Propulsion Group.
33. Groudle, T. A., "Sterilizable Monopropellant System," in *The Deep Space Network*, Space Programs Summary 37-47, Vol. III, Jet Propulsion Laboratory, Pasadena, Calif., Oct. 1967.